STUDY ON STRUCTURE, SURFACE MORPHOLOGY, ELECTRICAL AND MAGNETIC PROPERTIES IN MONOVALENT DOPED $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ AND $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ OF MAGNETIC CERAMICS

RABIATUL ADAWIYAH BINTI ZAWAWI

A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Science

Faculty of Applied Sciences and Technology
Universiti Tun Hussein Onn Malaysia

MARCH 2021

For my beloved parents Zawawi Jusoh and Shamsiah Zainal

ACKNOWLEDGEMENT

Alhamdulillah, all praises are belonging to Allah who has given the help and strength to complete my thesis successfully. May the blessing and peace of Allah be upon the messenger of Allah, Muhammad S.A.W. First of all, I would like to express my thanks to those who have been help me in conducting this research for their entire guide and helpful. Thus, in this opportunity I would like to express of gratitude to my supervisor, Dr. Suhadir bin Shamsuddin for his useful comment, guidance and kindly advice in making this research possible. I really appreciate his guidance from the initial to the final level that enabled me to develop an understanding of this research thoroughly. Not to forget, my co-supervisor, Dr. Norazila binti Ibrahim from School of Physics & Materials Studies, UiTM Shah Alam for her guidance and opinion in this research.

I am indebted to many other people who have helped me either directly or indirectly with this study. Then, special thanks to my friends and colleagues for their patience and cooperation during undertaking this research. Lastly, I would like greatly dedication and highly appreciation to my beloved parents and family for their continuous support and inspiration.

I also sincerely thank to Malaysian Ministry of Higher Education for providing the support of the sponsors under RAGS/1/2015/STD/UTHM/03/1 grant Vot R060 to do this project.

ABSTRACT

In perovskite manganites, Mn site substitution of Cr ion have attract great interest to suppress CO and induce phase transition. However most of study show inconsistent result regarding to the crystalline phase, surface morphology and magnetic properties as well as electrical properties study. Thus, two series of charge-ordered compound $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.04$) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ ($0 \leq y \leq 0.05$) manganites have been synthesized using solid-state reaction method and the crystalline phase, surface morphology and magnetic properties as well as electrical properties were reported. Cr^{3+} have been chosen in this study due the electronic configuration which similar to Mn^{4+} where it is possibly involved in double-exchange mechanism. X-ray diffraction analysis revealed the crystalline phase of all samples consists of essentially single phase and crystallized in an orthorhombic structure. The Cr doping were influence the lattice parameters and the unit cell volume, V whereas the values of V was observed to be decreased for both manganites series. Scanning electron microscope images of both compounds showed the changes of surface morphology for all samples when Cr was doped. AC susceptibility and DC electrical resistivity measurement for both parent compounds ($x = 0$ and $y = 0$) showed paramagnetic-insulator down to lower temperature. Interestingly, increasing of Cr for $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ compound showed ferromagnetic-metallic (FMM) transition for $x = 0.02$ and $x = 0.04$ samples. Metal-insulator transition temperature, T_{MI} were found to be T_{MI}~120 K and T_{MI}~122 K. Meanwhile for AC susceptibility measurement with Curie temperature, T_C increases from 132 K to 141 K respectively and undergoes the transition paramagnetic to ferromagnetic state. While, the $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ showed antiferromagnetic-insulator for $y = 0$, $y = 0.02$ and $y = 0.05$. Thus, the effect of Cr substitution on both manganites series showed significant results on crystalline phase, surface morphology and magnetic as well as electrical properties.

ABSTRAK

Dalam *perovskite* manganites, penggantian Cr pada bahagian Mn telah menarik minat besar untuk melemahkan CO dan menginduksi peralihan fasa. Walau bagaimanapun, kebanyakan kajian tidak menunjukkan keputusan yang stabil berhubung fasa kristal, permukaan morfologi dan sifat-sifat magnet serta elektrik. Oleh itu, dua siri sebatian caj $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.04$) dan $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ ($0 \leq y \leq 0.05$) manganites telah disintesis menggunakan kaedah tindak balas keadaan pepejal dan fasa kristal, permukaan morfologi dan sifat-sifat magnet serta elektrik dilaporkan. Cr^{3+} telah dipilih dalam kajian ini disebabkan oleh konfigurasi elektronik yang serupa dengan Mn^{4+} di mana ia mungkin terlibat dalam mekanisme *double-exchange*. Untuk kedua-dua siri manganites, analisis *X-ray diffraction* mendedahkan fasa kristal daripada semua sampel terdiri daripada fasa dasarnya tulen dan struktur berbentuk ortorombus. Peningkatan Cr mempengaruhi parameter kekisi dan unit isipadu sel, *V* manakala nilai-nilai *V* diperhatikan menurun untuk kedua-dua siri manganites. Imej dari *Scanning electron microscope* kedua-dua sebatian menunjukkan perubahan morfologi untuk semua sampel apabila didop Cr. Pengukuran *AC susceptibility and DC electrical resistivity* untuk kedua-dua sebatian tanpa dop Cr (x = 0 dan y = 0) menunjukkan sifat paramagnet-penebat ke suhu yang lebih rendah. Menariknya, peningkatan Cr untuk $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ menunjukkan peralihan feromagnet-logam (FMM) untuk sampel x = 0.02 dan x = 0.04. Suhu peralihan logam-penebat didapati sekitar T_{MI}~120 K and T_{MI}~122 K. Sementara itu, suhu Curie , T_C masing-masing meningkat daripada 132 K kepada 141 K dan mengalami peralihan paramagnet kepada feromagnet. Manakala, $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ menunjukkan sifat antiferromagnetic-penebat untuk y = 0, y = 0.02 dan y = 0.05. Oleh itu, kesan penggantian Cr di kedua-dua siri manganites menunjukkan kesan ke atas fasa kristal, permukaan morfologi dan sifat-sifat magnet serta elektrik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

ABO_3	-	Perovskite chemical formula
ACS	-	AC susceptibility
AFM	-	Antiferromagnetic
CMR	-	Colossal magneto-resistance
CO	-	Charge-order
CO_2	-	Carbon dioxide
Cr	-	Chromium
Cr_2O_3	-	Chromium (III) oxide
DCE	-	DC electrical
DE	-	Double exchange
e_g	-	Mobile electron
FESEM	-	Field emission scanning electron microscope
FM	-	Ferromagnetic
FMM	-	Ferromagnetic metallic
$h\ k\ l$	-	Miller indices
JT	-	Jahn Teller
Mn^{3+}	-	Magnesium (III) ion
Mn^{4+}	-	Magnesium (IV) ion
MnO_2	-	Manganese (IV) oxide
MnO_6	-	Manganese oxide octahedral
MR	-	Magnetoresistance
MI	-	Metal-insulator
Na^+	-	Sodium ion

Na_2CO_3	-	Sodium carbonate
Nd	-	Neodymium
Nd_2O_3	-	Neodymium (III) oxide
NNMCrO	-	$Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$
PMI	-	Paramagnetic insulating
PM	-	Paramagnetic
PNMCrO	-	$Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$
Pr	-	Praseodymium
Pr_2O_3	-	Praseodymium (III) oxide
$<r_A>$	-	Average ionic radius
SEM	-	Scanning electron microscope
T_C	-	Curie temperature
T_{CO}	-	Charge order temperature
T_{MI}	-	Metal insulator transition
XRD	-	X-ray diffraction

LIST OF APPENDICES

LIST OF PUBLICATIONS

Rabiatul Adawiyah Zawawi, Suhadir Shamsuddin & Nurul Nasuha Khairulzaman. (2017). Effect of Cr-doped on Crystalline Phase, Surface Morphology and Electrical Properties of Charge-Ordered $Nd_{0.75}Na_{0.25}MnO_3$ Ceramics. *Journal of Science and Technology*, 45-48.

Rabiatul Adawiyah Zawawi, Suhadir Shamsuddin & Norazila Ibrahim (2018). Enhancement of Double-Exchange Mechanism in Charge-Ordered $Pr_{0.75}Na_{0.25}MnO_3$ Ceramics by Cr Doped at Mn-Site. *International Journal of Current Science, Engineering & Technology*, 2581-4311.

Rabiatul Adawiyah Zawawi, Nurul Nasuha Khairulzaman, Suhadir Shamsuddin & Norazila Ibrahim (2018). Comparative Study on Structural, Electrical Transport and Magnetic Properties of Cr-Doped in Charge-Ordered $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ Manganites. *International Journal of Engineering & Technology*, 75-79.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Rare-earth manganites of the type of $Re_{1-x}A_xMnO_3$ (where R is a rare earth metal and A is monovalent/divalent alkali metal) has been studied previously due to the part of colossal magnetoresistance (CMR) effect and their potential technological application in electronic devices, magneto-electronic, photonic devices as well as infrared detector (Robler *et al*., 2011; Tokura *et al*., 1999; Vecherskii *et al*., 2002). In addition, several reports showed that substitution directly at Mn-sites with a certain amount of transition metal element affect the physical properties of the material, electron magnetic resonance and also charge ordering (CO) (Selmi *et al*., 2015; Thaljaoui *et al*., 2013). In this manganite compounds, charged ordering, lattice and spin are strongly combined, leading to exhibit various mechanism including to antiferromagnetic (AFM) super exchange, Jahn–Teller (JT) effect and charge ordering (CO) state which is interrelated with CMR effect (Yadav *et al*., 2012). In addition, studies on these rare-earth manganites have been revealed that CMR effect which is commonly attributed to the double exchange (DE) mechanism was also suggested to be related to the Jahn–Teller (JT) effect and charge ordering (CO) and the lattice distortion.

Recent studies progresses proved that the substitution of Re by A metal leads to a mixed valence of Mn^{3+} and Mn^{4+} state and induces a transition from paramagnetic-insulator to a ferromagnetic-metallic phase. The coexistence of the ferromagnetic state and metallicity has been explained using the double exchange (DE) mechanism which affected CO state and involve the mobility of e_g electrons to traveling between the Mn^{3+} and Mn^{4+} cations (Thaljaoui *et al*., 2013). For instance, for $Nd_{0.75}Na_{0.25}MnO_3$

below than 170 K the charge ordering start to develop (Li *et al*., 2004) and for $Pr_{0.75}Na_{0.25}MnO_3$, the CO start to develop below than 220 K after the electron diffraction experiment was carried out which showed the super-lattice diffraction appear below 220 K (Zhang *et al*., 2005). According to previous study by Liu *et al*., 2007 on substitution of Mn by Co in $Nd_{0.5}Ca_{0.5}MnO_3$ induced ferromagnetic-paramagnetic and metal insulator (MI) transition at low temperature as well as suppresses the CO state. Meanwhile, further studies demonstrated monovalent substitution can affect the physical properties (Li *et al*., 2004; M'Nassri *et al*., 2005). Previous study reported on substitution of sodium (Na) as a monovalent-doped on the properties of the $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ (Li *et al*., 2007) have shown the resistivity values decreases with Fe content up to $x \leq 0.05$, and then increases subsequently with further Fe doping indicating a suppression of double exchange (DE) mechanism. Meanwhile, previous study on $Pr_{0.8}Na_{0.2}Mn_{1-x}Co_xO_3$ shows the composition of $x = 0.04$ induced a MI transition connected with a ferromagnetic (FM) arrangement (Pollert *et al*., 2003). Hence, substitution of magnetic ion at Mn-site has shown interesting inducement of phase transition as well as influencing the CO state. However, study on monovalent-doped manganites is still unsatisfactory.

The Cr^{3+} ion is a very effective element to suppress CO and induced magnetic transition. Cr doping of half-doped manganite also reveals a lot of anomalous magnetic and electrical transport properties. For example in $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ manganite, the CO occurred below 170 K. Then, when Cr ion was doped, the CO transition and ferromagnetic (FM) ordering was changed as Curie temperature, T_C increased from 150 K to 153 K for $x = 0.02$ and $x = 0.05$ respectively. These changes were suggested due to the effect of DE interaction between Mn^{3+} and Cr^{3+}. Furthermore, both electrical resistivity and magnetic susceptibility measurement was showed that the CO insulating and FM metallic phases coexist in the $Nd_{0.5}Ca_{0.5}MnO_3$ compound (Carneiro *et al*., 2003). Other than that, increasing of Cr doped up to $x = 0.07$ for $La_{0.8}Ca_{0.2}Mn_{1-x}Cr_xO_3$ compound caused a MI transition to shifted to lower temperature (Manjunatha *et al*., 2016). Thus, considering all the above, the studies on the effect of Cr doping on Mn site was expected to understand the physical nature of doping effect in manganites. However, the number of such studies on substitution at Mn-site in monovalent-doped manganites is still limited. Hence, in this study, the chromium (Cr) with charge three positive ions was doped into the Mn-site of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganite series in order to investigate the effect on the structure properties, surface morphology and electrical properties as well as magnetic properties in monovalent doped manganite.

1.2 Problem statement

The praseodymium (Pr) and neodymium (Nd) ion with cationic radii smaller as compared to lanthanum (La) was caught attention among rare earth element family that lead to reduce the band width of e_g electrons and various average ionic radius (Thaljaoui *et al*., 2013). $Nd_{0.75}Na_{0.25}MnO_3$ (Li *et al*., 2004) and $Pr_{0.75}Na_{0.25}MnO_3$ (Zhang *et al*., 2005) displays the existence of the charge ordered where the charge ordering (CO) transition for the both compound occur at temperature around 180 K and 220 K respectively. Many reports showed that substitution small amount of transition-metal element at Mn-site have a very effective ways to alter the properties of materials due to the changes of Mn^{3+}/ Mn^{4+} ratio. Based on previous study by Arifin *et al*., 2018 parent compound (x = 0) of $Nd_{0.75}Na_{0.25}MnO_3$ exhibited insulating behavior. Then, it was induced to metallic behavior when Ni ion was doped at Mn site suggested due to the enhancement of double-exchange (DE) mechanism as well as weakening the CO state.

Meanwhile, electrical resistivity measurement by Rozilah *et al*., 2017 for parent compound of $Pr_{0.75}Na_{0.25}MnO_3$ also exhibit as insulating behavior. Then, when some amount of K ion was doped, metal-insulator transition was showed due to double exchange interaction. Study by Sun *et al*., 2001 shows all samples for Cr doped up to 0.3 in compound of $La_{0.67}Ca_{0.33}Mn_{1-x}Cr_xO_3$ exhibit a ferromagnetic-paramagnetic (FM-PM) transition with T_C decreased with increasing of Cr content for $x \leq 0.2$. Cr has been chosen in this study because of the Cr ion would be suggested to suppress the CO and induce magnetic transition as well as reveal a significance information on anomalous magnetic and electrical phenomena (Zhang *et al*., 2011). Cr^{3+} have been suggested to play a similar role as Mn^{4+} since Cr^{3+} has the same electronic configuration with Mn^{4+} then it is possible that the Cr^{3+} ion may interact with Mn^{3+} ion and induce ferromagnetic-metallic (FMM) state as reported by (Modi *et al*., 2016; Gao *et al*., 2007) and this study suggested that Cr could promote the development of FMM due to the effect of DE mechanism of Mn^{3+}–O–Mn^{4+}.

Apart from that, Cr ion was known as the most efficient one to induce a metal insulator transition phenomena (Zhang *et al*., 2011; Manjunatha *et al*., 2016) however most of the substitution of Cr doping on Mn-site does not show full suppression of FMM phases probably due to low dopant levels. Hence, by doping a variable small amount of charged ions at Mn site could change some properties of a material such as structure and electrical properties as well as magnetic properties. Moreover, such study on $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ compound is still limited and to the best of our knowledge, study on the $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ compound has not been previously reported.

1.3 Objectives of study

In this research, systematic studies on investigating the influence of elemental substitutions of monovalent-doped $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganites were carried out.

The main objectives of this research are as follows:

i. To investigate the effect of Cr doping on crystalline phase and surface morphology using X-ray diffraction (XRD) measurement and scanning electron microscope (SEM) in $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganites respectively.

ii. To investigate the effect of Cr doping on electrical properties in $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganites using DC electrical resistivity measurement.

iii. To elucidate the influence of Cr doping in $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganites on magnetic properties using AC susceptibility measurement at low temperature.

1.4 Scope of study

In this research, perovskite manganites of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (PNMCrO) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ (NNMCrO) were prepared using solid-state synthesis method. A stoichiometric amount of Pr_2O_3, Nd_2O_3, Na_2CO_3, MnO_2 and Cr_2O_3 powders with high purity (≥99.99%) undergoes the process of mixing, calcination, and pelleting as well as sintering process. The structural investigations using powder X-ray diffraction (XRD) Bruker D8 Advance system with Cu Kα radiation at room temperature was used in order to identify the crystallinity phase of the material. The study on the surface morphology of PNMCrO and NNMCrO has been conducted using scanning electron microscope (SEM). From this technique, the information on grain boundaries, grain size and porosity has been explained. Then, results from the DC electrical resistivity measurements utilized using four-point-probe method in temperature range of 50 K to 300 K also were characterized to investigate the electrical properties. Magnetic measurements were also performed at low temperature measurement to elucidate the magnetic properties using magnetic AC susceptibility measurement.

1.5 Significance of study

There are several ways to investigate the mechanism of the transition metal oxides especially the rare-earth (RE) manganite such as ferromagnetic-metallic (FMM) transition, Jahn–Teller (JT) effect, double exchange (DE) and charge ordering (CO) state which is interrelated with CMR effect. However up to now, the mechanism of rare-earth manganite is still not clearly understood. Hopefully, this research will provide some information about the idea of mechanisms on this compound. Several reports showed that elemental substitution at B-site plays a crucial role in influencing electro-magnetic of the RE manganite. Thus, this study has been focusing on the Cr doping at Mn-site of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ manganite with the hope to provide a better understanding on the physical properties of materials towards the potential application such as in magnetic field sensor as well as communication devices. In addition, it is an important to reveal the effect of Cr doping on the structure and electro-magnetic properties related the CO state. The presence of a CO state below *Tc* is commonly accompanied with the presence of antiferromagnetic (AFM) state (Mno *et al*., 2011; Reis *et al*., 2005; Yadav *et al*., 2012). The appearance of CO state in monovalent-doped manganite systems, such as Fe doped at Mn site in $Pr_{0.75}Na_{0.25}Mn_{0.9}Fe_{0.1}O_3$ suppresses the CO state and revives the FMM state (Qian *et al*., 2006). Hence, this study is important in order to determine the physical properties of the materials by substitution of monovalent ions at Mn site in this Pr-based and Nd-based significantly induced the magnetic properties from ferromagnetic to paramagnetic phase and the electrical properties which are metal–insulator (MI) transition at low temperature measurement.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter literally introduces about the summarized information of the relevant studies on research related to chromium (Cr) being doped with the manganites. It elucidates the effect of Cr doping on the structure, surface morphology and magnetic as well as electrical properties in monovalent and divalent doped of manganites. Then, the overview of previous study and research based on journals and articles which include ceramic concept and the theoretical parts that related with this research. In this study, Cr has been chosen as monovalent element to doped with parent compound of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Cr_yO_3$ at Mn site. Perovskite manganites with the general formula $Re_{1-x}A_xMnO_3$ (where R is a rare earth metal such as La^{3+}, Pr^{3+} etc. and A is monovalent/divalent alkali metal such as Ca^{2+}, Sr^{2+}) have gained interest due to simultaneous occurrence of transition from ferromagnetic (FM) to paramagnetic (PM) behavior at Curie temperature (T_C) and metal to insulator transition at metal-insulator temperature (T_{MI}). In manganite, ferromagnetic-metallic (FMM) behaviors are explained by double exchange (DE) interaction which involves an interaction between two pair of ions Mn^{3+} and Mn^{4+}. Meanwhile for paramagnetic-metal insulator (PMI) transition can be explained by Jahn-Teller effect. Moreover, substitution on Mn-site is found to be effective way to alter the properties. Therefore, this chapter was important as guidance and reference to accomplish this research.

2.2 Theoretical of research

Perovskite structure is an oxide-based compound made by a combination of two or more crystalline structure bonded with oxygen. Permanently, it stands with chemical formula ABX_3 where A and B represent metallic cations with different sizes and X is non-metallic anions usually composed of oxygen and become edge centers to both A and B respectively. In manganites with a metal-insulator transition, the metallic state and ferromagnetic state are coupled, which is explained by the double exchange theory. This exchange is ferromagnetic in nature and metallic since if the core electrons of 3d shells of two Mn^{3+} and Mn^{4+} neighbors are ferromagnetically aligned, then the e_g electron of the Mn^{3+} can easily hop onto the empty e_g orbital of its neighbor. This roughly explains why, below their ferromagnetic transition temperature (T_C), the manganites become metallic whereas above T_C a paramagnetic state.

2.2.1 Perovskite structure, ABO_3

A perovskite can be defined as combination of crystalline structure and manganese-base in which any material that have same type of crystal structure as $PrMnO_3$ and $CaTiO_3$. The general formula for perovskite compounds is ABO_3 with oxygen in the face centers, where 'A' and 'B' are cations with different sizes, and O is an anion that bonds to both cation. In these case 'A' atoms must be larger than the 'B' atoms.

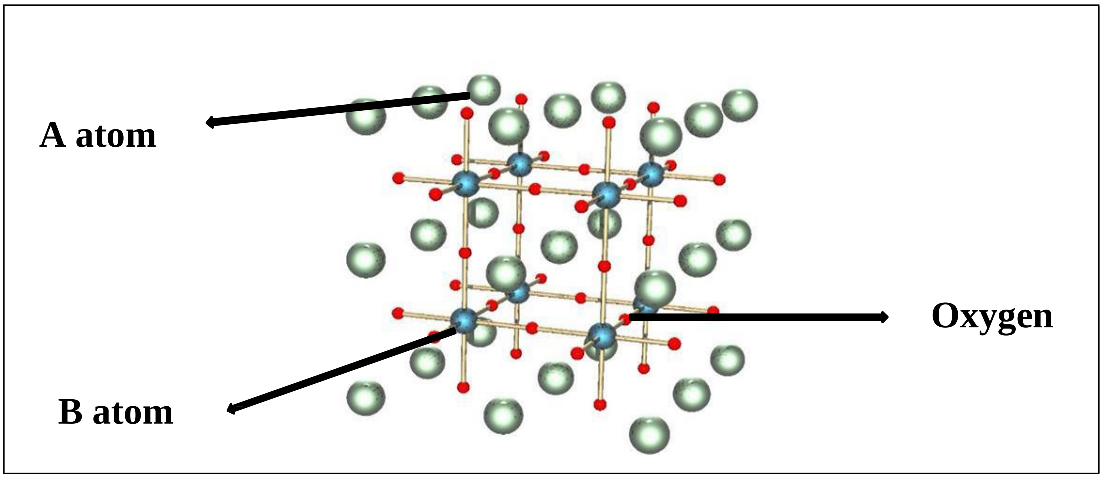

Figure 2.1: Structure of perovskite. Green spheres represent the A cations, blue spheres represent the B cations, with red spheres representing oxygen ions. (Chun-hua *et al*., 2002)

REFERENCES

Abdullah, H. & Halim, S. A. (2010). Disorder Phenomena in Nd-doped. *Sains Malaysiana*, *39*(1), 93–98.

Arifin, M., Ibrahim, N., Mohamed, Z., Yahya, A. K., Khan, N. A., & Khan, M. N. (2018). Revival of Metal-Insulator and Ferromagnetic-Paramagnetic Transitions by Ni Substitution at Mn Site in Charge-Ordered Monovalent Doped $Nd_{0.75}Na_{0.25}MnO_3$ Manganites. *Journal of Superconductivity and Novel Magnetism*, *31*(9), 2851–2868.

Asmira, N., Ibrahim, N., Mohamed, Z., & Yahya, A. K. (2018). Effect of Cr^{3+} substitution at Mn-site on electrical and magnetic properties of charge ordered $Bi_{0.3}Pr_{0.3}Ca_{0.4}MnO_3$ manganites. *Physica B: Condensed Matter*, *544*, 34-46.

Bettaibi, A., M'Nassri, R., Selmi, A., Rahmouni, H., Chniba-Boudjada, N., Cheikhrouhou, A., & Khirouni, K. (2015). Effect of chromium concentration on the structural, magnetic and electrical properties of praseodymium-calcium manganite. *Journal of Alloys and Compounds*, *650*, 268–276.

Carneiro, A. S., Fonseca, F. C., Jardim, R. F., & Kimura, T. (2003). Phase coexistence in Cr-doped $Nd_{0.5}Ca_{0.5}MnO_3$ compounds. *Journal of Applied Physics*, *93*(103), 8074–8076.

Chin, H. W., & Cheong, K. H. (2015). Effect of Sintering on Structural and Transport Properties on Nanosized, *Trans Tech Publication*, *1107*, 272–277.

Chun-hua, H. Yun L., & Chun S. L. (2002). Structural Dependence of Magnetic and Transport Properties in Doped Manganite Perovskites *Journal of Structural Chemistry*, *21*(3), 233-240.

Elyana, E., Mohamed, Z., Kamil, S. A., Supardan, S. N., Chen, S. K., & Yahya, A. K. (2018). Revival of ferromagnetic behavior in charge-ordered $Pr_{0.75}Na_{0.25}MnO_3$ manganite by ruthenium doping at Mn site and its MR effect. *Journal of Solid State Chemistry*, *258*, 191–200.

Gamzatov, A. G., Batdalov, A. B., & Kamilov, I. K. (2011). Correlation of electrical and thermalphysical properties of $La_{0.85}Ag_{0.15}MnO_3$ manganite. *Physica B: Condensed Matter*, *406*(11), 2231–2234.

Gao, H. P., Wu, B. M., & Li, B. (2007). Effect of Cr-doping on thermal transport property in perovskite $R_{0.7}A_{0.3}Mn_{1-x}Cr_xO_3$. *Physica B: Condensed Matter, 389*(2), 252–257.

Gao, T., Cao, S., Li, W., Kang, B., Yu, L., Yuan, S., & Zhang, J. (2009). Spin glass behavior in the half doped $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ system. *Physica B: Condensed Matter, 404(8-11),* 1283-1286.

Hcini, S., Zemni, S., Triki, A., Rahmouni, H., & Boudard, M. (2011). Size mismatch , grain boundary and bandwidth effects on structural , magnetic, and electrical properties of $Pr_{0.67}Ba_{0.33}MnO_3$ and $Pr_{0.67}Sr_{0.33}MnO_3$ perovskite. *Journal of Alloys and Compounds*, *509*, 1394–1400.

Kahn, M. L., Hlil, E. K., Ellouze, M., Elhalouani, F., Sbissi, K., & Collie, V. (2015). Fe doping effects on the structural , magnetic , and magnetocaloric properties of nano-sized. *Journal of Nanostruct Chem*, *3*, 313-323.

Kalyana Lakshmi, Y., Manjunathrao, S., & Venugopal Reddy, P. (2014). Influence of rare-earth ion doping on magnetotransport behavior of potassium doped manganites. *Materials Chemistry and Physics*, *143*(3), 983–990.

Kansara, S. B., Dhruv, D., Kataria, B., Thaker, C. M., Rayaprol, S., Prajapat, C. L., Shah, N. A. (2015). Structural, transport and magnetic properties of monovalent doped $La_{1-x}Na_xMnO_3$ manganites. *Ceramics International*, *41*(5), 7162–7173.

Khursheed A. (2011). Conventional SEM Design. *Scanning Electron Microscope and Spectrometers*, 1–71.

Li, H. (2008). Synthesis of CMR manganites and ordering phenomena in complex transition metal oxides, 176.

Li, Y., Miao, J., Sui, Y., Wang, X., Zhang, W., Liu, Y., Su, W. (2007). Synthesis, structural and transport properties of $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0.0 \leq x \leq 0.3$). *Journal of Alloys and Compounds*, *441*(1–2), 1–5.

Li, Z. Q., Zhang, X. H., Yu, J. S., Liu, X. J., Liu, X. D., Liu, H., Jiang, E. Y. (2004). Competition between the charge ordered and ferromagnetic states in $(La,Nd)_{0.75}Na_{0.25}MnO_3$ manganites. *Physics Letters, Section A: General, Atomic and Solid State Physics*, *325*(5–6), 430–434.

Liu, Y. K., Yin, Y.W., Li, X. G. (2013). Colossal magnetoresistance in manganites and related prototype devices. *Chinese Physics B*, *22*(8), 87502.

Maatar, S. C., M'Nassri, R., Koubaa, W. C., Koubaa, M., & Cheikhrouhou, A. (2015). Structural, magnetic and magnetocaloric properties of $La_{0.8}Ca_{0.2-x}Na_xMnO_3$ manganites. *Journal of Solid State Chemistry*, *225*, 83–88.

Manjunatha, S. O., Rao, A., Babu, P. D., Chand, T., & Okram, G. S. (2016). Electric, magnetic, and thermo-electric properties of Cr doped $La_{0.8}Ca_{0.2}Mn_{1-x}Cr_xMnO_3$ manganites. *Solid State Communications*, *239*, 37–43.

Manjunatha, S. O., Rao, A., Babu, P. D., Tarachand, & Okram, G. S. (2015). Studies on magneto-resistance, magnetization and thermoelectric power of Cr substituted $La_{0.65}Ca_{0.35}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.07$) manganites. *Physica B: Condensed Matter*, *475*, 1–9.

Mehri, A., Cheikh-Rouhou Koubaa, W., Koubaa, M., & Cheikh-Rouhou, A. (2009). Effect of sodium substitution on the structural, magnetic and magnetocaloric properties of $La_{0.5}Ca_{0.5}MnO_3$ perovskite manganites. *Physics Procedia*, *2*(3), 975–982.

Mno, N. C. (2011). Effect of Ru-substitution on electrical and magnetocaloric properties of. *Solid State Communications*, *151*(2), 107–111.

Modi, A., Bhat, M. A., Bhattacharya, S., & Gaur, N. K. (2016). Investigation of structural and some physical properties of Cr substituted polycrystalline $Eu_{0.5}Sr_{0.5}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.1$) manganites. *Journal of Materials Science: Materials in Electronics*, *27*(9), 8899–8905.

Modi, A., & Gaur, N. K. (2015). Structural, electrical and magnetic phase evolution of Cr substituted $GdMn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.2$) manganites. *Journal of Alloys and Compounds*, *644*, 575–581.

Mucha, J., & Cheikhrouhou, A. (2013). Structural , magnetic and transport study of monovalent Na-doped manganite, *Journal of Alloys and Compounds*, *558*, 236–243.

Phong, P. T., Khien, N. V, Dang, N. V, Manh, D. H., Hong, L. V, & Lee, I. (2015). Effect of pb substitution on structural and electrical transport of $La_{0.7}Ca_{0.3}À_xPb_x$ MnO_3 ($0 \leq x \leq 0.3$) manganites. *Physica B: Physics of Condensed Matter*, *466–467*, 44–49.

Pi, L., Hébert, S., Yaicle, C., Martin, C., Maignan, A., & Raveau, B. (2003). The $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ series ($0 \leq x \leq 0.5$): Evidence of steps in the magnetic and transport properties for a narrow composition range. *Journal of Physics Condensed Matter*, *15*(17), 2701–2709.

Pollert, E., Hejtmánek, J., Jirák, Z., Knížek, K., & Maryško, M. (2003). Influence of Co doping on properties of $Pr_{0.8}Na_{0.2}Mn_{1-y}Co_yO_3$ perovskites. *Journal of Solid State Chemistry*, *174*(2), 466–470.

Qian, Z., & Su, W. (2006). Phase separation, low-field magnetic and transport properties of $Pr_{0.75}Na_{0.25}Mn_{0.9}Fe_{0.1}O_3$. *Journal of Magnetism and Magnetic Materials*, *305*, 247–252.

Ramay, S. M., Mahmood, A., Atiq, S., & Alhazaa, A. N. (2016). Study of divalent elements (Mg, Sr and Ba)-doped $LaMnO_3$ nano-manganites. *International Journal of Modern Physics B, 30*, 1–9.

Ramos, A. Y., Tolentino, H. C. N., Soares, M. M., Grenier, S., Bunău, O., Joly, Y., Caneiro, A. (2013). Emergence of ferromagnetism and Jahn-Teller distortion in $LaMn_{1-x}Cr_xO_3$ (x<0.15). *Physical Review B - Condensed Matter and Materials Physics*, *87*(22), 1–8.

Rebello, A. (2010). Colossal Electroresistance, Magnetoimpedance, and Magnetocaloric Effects in Selected Manganites. *Most*.

Reis, M. S., Gomes, A. M., Arau, J. P., Amaral, J. S., & Tavares, P. B. (2005). Charge-ordering contribution to the magnetic entropy change of $PrCaMnO_3$ manganites. *Journal of Magnetism and Magnetic Materials, 291*, 697–699.

Rößler, S., Nair, H. S., Rößler, U. K., Kumar, C. M. N., Elizabeth, S., & Wirth, S. (2011). Ferromagnetic transition and specific heat of $Pr_{0.6}Sr_{0.4}MnO_3$. *Physical Review B, 84*(18), 184422.

Rozilah, R., Ibrahim, N., Mohamed, Z., Yahya, A. K., Khan, N. A., & Khan, M. N. (2017). Inducement of ferromagnetic-metallic phase in intermediate-doped charge-ordered $Pr_{0.75}Na_{0.25}MnO_3$ manganite by K^+ substitution. *Physica B: Condensed Matter*, *521*, 281–294.

Schultz, L., R. von Helmolt., B. Holzapfel., Samwer, K,. (1993). Giant negative magnetoresistance in perovskitelike $La_{2/3}Ba_{1/3}MnO_x$. *Physical Review Letters, 71(14)*, 2331–2333.

Selmi, A., Bettaibi, A., Rahmouni, H., M'nassri, R., Chniba Boudjada, N., Chiekhrouhou, A., & Khirouni, K. (2015). Physical properties of 20% Cr-doped $Pr_{0.7}Ca_{0.3}MnO_3$ perovskite. *Ceramics International*, *41*(9), 11221–11227.

Shaikh, M. W., Mansuri, I., Dar, M. A., & Varshney, D. (2015). Materials Science in Semiconductor Processing Structural and transport properties of $La_{1-x}Ag_xMnO_3$ (x = 0.075, 0.1, 0.125 and 0.15) manganites, *35*, 10–21.

Shamsuddin, S., Ibrahim, A. M. A., & Yahya, A. K. (2013a). Effect of Er substitution on ultrasonic anomaly in $Dy_{0.5-x}Er_xBa_{0.5}CoO_3$ cobaltates. *Ultrasonics*, *53*(6), 1084–1088.

Shamsuddin, S., Ibrahim, A. M. A., & Yahya, A. K. (2013b). Effects of Cr substitution and oxygen reduction on elastic anomaly and ultrasonic velocity in charge-ordered $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_{3-\delta}$ ceramics. *Ceramics International*, *39*, S185–S188.

Singh, D., & Mahajan, A. (2015). Investigation of structural, magnetic and electric transport properties of half-doped chromium manganites $La_{0.3}R_{0.2}Sr_{0.5}Mn_{0.5}Cr_{0.5}O_3$ (R=La, Nd, Sm, and Gd). *Ceramics International*, *41*(9), 11748–11755.

Siwach, P. K., Singh, H., & Srivastava, O. N. (2008). Low field magnetotransport in manganites. *Journal of Physics. Condensed Matter : An Institute of Physics Journal*, *20*, 273201.

Sudyoadsuk, T., Suryanarayanan, R., Winotai, P., & Wenger, L. E. (2004). Suppression of charge-ordering and appearance of magnetoresistance in a spin-cluster glass manganite $La_{0.3}Ca_{0.7}Mn_{0.8}Cr_{0.2}O_3$. *Journal of Magnetism and Magnetic Materials*, *278*(1–2), 96–106.

Sun, Y., Xu, X., & Zhang, Y. (2001). Effects of Cr doping in $La_{0.67}Ca_{0.33}MnO_3$: Magnetization, resistivity, and thermopower. *Physical Review B - Condensed Matter and Materials Physics*, *63*(5), 1–5.

Tang, F. L., Huang, M., Lu, W. J., & Yu, W. Y. (2009). Structural relaxation and Jahn–Teller distortion of $LaMnO_3$ (001) surface. *Surface Science*, *603*(6), 949–954.

Thaljaoui, R., Boujelben, W., Pękała, K., Pękała, M., Cheikhrouhou-Koubaa, W., & Cheikhrouhou, A. (2013). Magnetocaloric study of monovalent-doped manganites $Pr_{0.6}Sr_{0.4-x}Na_xMnO_3$ ($0 \leq x \leq 0.2$). *Journal of Materials Science*, *48*(11), 3894–3903.

Thaljaoui, R., Boujelben, W., Pękała, M., Pękała, K., & Cheikhrouhou, A. (2013). Structural and Electrical Properties of Monovalent Doped Manganites $Pr_{0.6}Sr_{0.4-x}K_xMnO_3$ (x = 0, 0.05 and 0.1). *Journal of Superconductivity and Novel Magnetism*, *26*(5), 1625–1630.

Tokura, Y., & Tomioka, Y. (1999). Colossal magnetoresistive manganites. *Journal of Magnetism and Magnetic Materials*, *200*(1–3), 1–23.

Vecherskii, S. I., Konopel, M. A., Esina, N. O., & Batalov, N. N. (2002). Transport Properties of $Ca_{1-x}MnO_{3-\delta+x}CeO_2$ ($0<x\leq 0.15$) Mixtures. *Inorganic Materials*, *38*(12), 1270–1276.

Walha, I., & Cheikhrouhou, A. (2009). The effect of calcium and praseodymium deficiencies on the physical properties of $Pr_{0.5}Ca_{0.5}MnO_3$. *Physics Procedia*, *2*(3), 953–960.

Xiao, X., Yuan, S., Yin, S., Chen, L., Ren, G., Miao, J., & Yu, G. (2008). Electrical transport and magnetic properties of $La_{0.67}Ca_{0.33}Mn_{1-x}Cr_xO_3$ and $La_{0.67+x}Ca_{0.33-x}Mn_{1-x}Cr_xO_3$($0.04\leq x\leq 0.08$). *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, *23*(4), 463–466.

Xinghua, Z., & Zhiqing, L. I. (2011). Influence of Cr-doping on the magnetic and electrical transport properties of. *Journal of Rare Earths*, *29*(3), 230–234.

Yadav, K., Vaithyanathan, V., Inbanathan, S. S. R., & Varma, G. D. (2012). Magnetic and charge ordering properties of $Bi_{0.2}Ca_{0.8}Mn_{0.9}X_{0.1}O_3$ (where X=Ti, Cr, Fe, Co, Ni, Cu). *Journal of Alloys and Compounds*, *533*, 19–24.

Zener, C. (1951). Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with Perovskite structure. *Physical Review*, *82*(3), 403–405.

Zhang, X. H., Li, Z. Q., Song, W., Du, X. W., Wu, P., Bai, H. L., & Jiang, E. Y. (2005). Magnetic properties and charge ordering in $Pr_{0.75}Na_{0.25}MnO_3$ manganite. *Solid State Communications*, *135*(6), 356–360.

Zhang, X., & Li, Z. (2011). Influence of Cr-doping on the magnetic and electrical transport properties of $Nd_{0.75}Na_{0.25}MnO_3$. *Journal of Rare Earths*, *29*(3), 230–234.

Zhou, H., Li, G., Chen, H., Zheng, R., Fan, X., & Li, X. (2001). The Jahn – Teller effect and electron – phonon. *Journal of Physics Condensed matter*, 6195-6202.